Electronic Supplementary Material (ESI) for RSC Advances

Supplementary Information for

Synthesis of Transuranium-Based Nanocrystals via the Thermal Decomposition of Actinyl Nitrates.

D. Hudry, C. Apostolidis, O. Walter, T. Gouder, A. Janssen, E. Courtois, C. Kübel and D. Meyer*

Experimental Section

Caution: Because uranium (natural uranium) and neptunium (^{237}Np) are used in this study, usual precautions for working with radioactive materials should be followed. All experiments involving ^{237}Np have been performed in a dedicated glove boxe.

Chemicals: Benzyl ether (BnOBn, 99%, Acros Organics), oleic acid (OA, Ph. Eu., Fluka), Oleylamine (OAm, 80 – 90% C18 content, Acros Organics), ethanol (absolute, Merck) and toluene (min 99.7%, Sigma-Aldrich) were used as received without further purification. Uranyl nitrate ($UO_2(NO_3)_2$*$6H_2O$) was purchased from Merck and used as received.

Synthesis of $NpO_2(NO_3)_2$*$3H_2O$ (manuscript in preparation)**:** 200 mg of NpO_2 (ITU's stock) were dissolved in 4 mL of concentrated nitric acid (14M). The mixture is kept at a gentle boil until a clear pink solution to be obtained. The oxidation of Np(IV) to Np(VI) is checked by UV-VIS spectroscopy. The as-obtained Np(VI) nitric solution is then concentrated by evaporation (final volume ≈ 1 mL). Crystals suitable for x-ray diffraction were evident in the solution the following day. $NpO_2(NO_3)_2$*$3H_2O$ has been characterised by single crystal XRD (Bruker Apex II Quazar system) leading to a triclinic (space group P-1) elementary cell with the following parameters: a = 5.6973(3) Å, b = 6.4675(4) Å, c = 7.0094(4) Å, alpha = 109.9610(10), beta = 98.4810(10), gamma = 109.1920(10) clearly showing its consistency as $NpO_2(NO_3)_2$*$3H_2O$ in agreement with the data reported by Steinhauser *[M. Steinhauser, Dissertation der Fakultät für Chemie und Pharmazie der Ludwig-Maximilians-Universität, 1987 (in German)]*. Evidence for Np(VI) is given by its UV-VIS spectrum (i.e. absorption band at 1222 nm) in agreement with the data

reported in the literature *[1. J. Inorg. Nucl. Chem. 1980, 42, 1347 and 1349 / 2. C. Apostolidis, H. Bokelund, M. Ougier, Speciation of Neptunium in concentrated nitric acid: absorption spectra of Np(IV), Np(V) and Np(VI) in 18èmes Journées des Actinides, April 20-22, 1988, Paris]*. Crystals (≈ 5 mm) were recovered and dried with an adsorbing tissue and directly used in the synthesis of NpO_2 nanocrystals.

Synthesis of uranium oxide nanocrystals: The synthesis is performed using air-free techniques under purified argon atmosphere. BnOBn (1500 µL – 8 mmol), OA (242 µL – 0.8 mmol) and $UO_2(NO3)_2.6H_2O$ (39.4 mg – 0.08 mmol) are introduced into a three-neck flask at room temperature. The resulting mixture is heated up to 150°C for 15 min in order to dissolve $UO_2(NO_3)_2.6H_2O$. When a clear orange/brown solution is obtained, the mixture is cooled down to 100°C and OAm is added (254 µL – 0.8 mmol). The resulting solution is degassed under vacuum (5.10^{-2} mbar) at 100°C for 20 minutes. The mixture is then successively heated up (10°C/min) to 220°C and 280°C, and kept at each temperature for 30 minutes. Afterwards, the heating mantle is removed and the flask is left to cool naturally to room temperature.

Synthesis of neptunium oxide nanocrystals: The synthesis is performed using air-free techniques under purified argon atmosphere in a glove box. BnOBn (1500 µL – 8 mmol), OA (242 µL – 0.8 mmol) and $NpO_2(NO3)_2.3H_2O$ (32.8 mg – 0.08 mmol) are introduced into a three-neck flask at room temperature. The resulting mixture is heated up to 150°C for 15 min in order to dissolve $NpO_2(NO_3)_2.3H_2O$. When a clear brown solution is obtained, the mixture is cooled down to 100°C and OAm is added (254 µL – 0.8 mmol). The resulting solution is degassed under vacuum (5.10^{-2} mbar) at 100°C for 20

minutes. The mixture is then successively heated up (10°C/min) to 220°C and 280°C, and kept at each temperature for 30 minutes. Afterwards, the heating mantle is removed and the flask is left to cool naturally to room temperature.

Nanocrystals recovering and purification procedure. Absolute ethanol is added to the uranium solution at room temperature. The initial clear solution turn black turbid immediately. After centrifuging (4000 rpm, 5 min) the clear supernatant is discarded and the resulting black precipitate is dispersed in toluene. This purification procedure (ethanol precipitation – centrifuging – toluene dispersion) is repeated three times to remove all residual organics. For the last purification cycle, the final toluene solution is centrifuged 20 min at 8000 rpm. The final clear black solution is kept in a glass vial.

The neptunium oxide nanocrystals are recovered according to a similar procedure. Nevertheless, for safety reasons the ethanol solutions containing the neptunium oxide nanocrystals are not centrifuged. With time (2 hours), a white brown precipitate settled down to the flask. This purification procedure (ethanol precipitation – toluene dispersion) is repeated three times. The final clear yellow solution is kept in a glass vial.

Characterization techniques: XRD was performed at room temperature in Bragg-Brentano geometry using a Bruker D8 Advance powder diffractometer with a copper anticathode and a (111) Ge monochromator. The D8 Advance is equipped with a 1-dimensional detector (LynxEye). XRD patterns were recorded in the range 10° - 120° with a step size of 0.03° and a counting time of 15 s per step. Rietveld refinement was performed using Jana 2006 software with the fundamental approach method. XRD samples were

prepared by drop-casting solutions of uranium or neptunium oxide nanocrystals dispersed in toluene onto a (911)-oriented silicon substrate.

Transmission electron microscopy (TEM) analysis of uranium oxide nanocrystals was performed using an image corrected FEI Titan 80-300 microscope operated at 300 kV and equipped with a Gatan US1000 CCD camera for TEM imaging. Scanning transmission electron microscopy (STEM) images were acquired using HAADF (High Angle Annular Dark Field) detector with a nominal spot size of 0.14 nm.

Transmission electron microscopy (TEM) analysis of neptunium oxide nanocrystals were conducted with a specially modified FEI Tecnai G^2 F20 XT for the analyses of radioactive materials. The TEM is operating at 200 kV and equipped with a Gatan US1000 CCD camera for TEM imaging. To avoid radioactive contamination during the sample transfer, a glove box with controlled atmosphere is mounted around the FEI CompuStage (Figure S1).

TEM samples were prepared by drop-casting diluted suspensions of the nanocrystals in toluene onto carbon coated copper grids (Quantifoil holey carbon grids coated with a 2 nm thickness carbon layer).

FTIR spectra of the uranium and neptunium oxide nanocrystals were collected on a PerkinElmer spectrometer (Spectrum 400 FTIR/FTFIR). A drop of solutions of uranium or neptunium oxide nanocrystals dispersed in toluene was mixed with KBr and compressed into a pellet at 9000 psi.

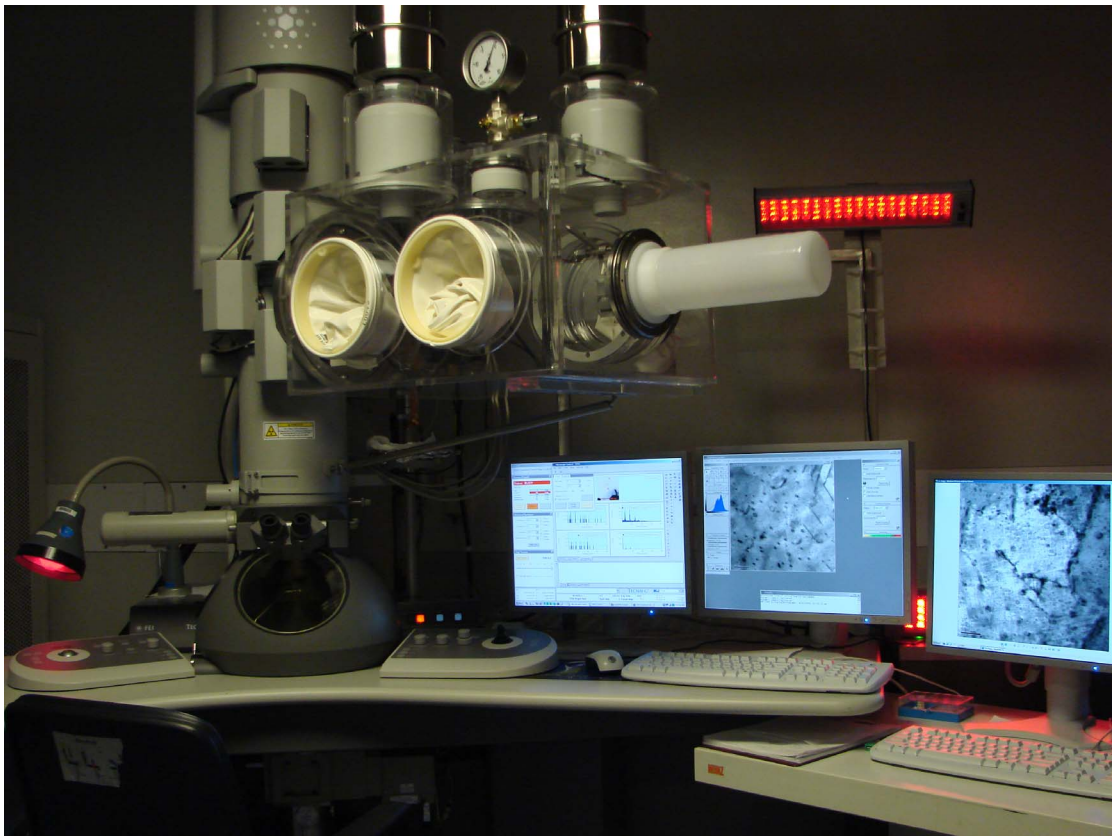

Figure S1. ITU's modified TEM dedicated to the analysis of radioactive materials (including irradiated fuels). The TEM samples are prepared and mounted on the sample holder in another glove box.

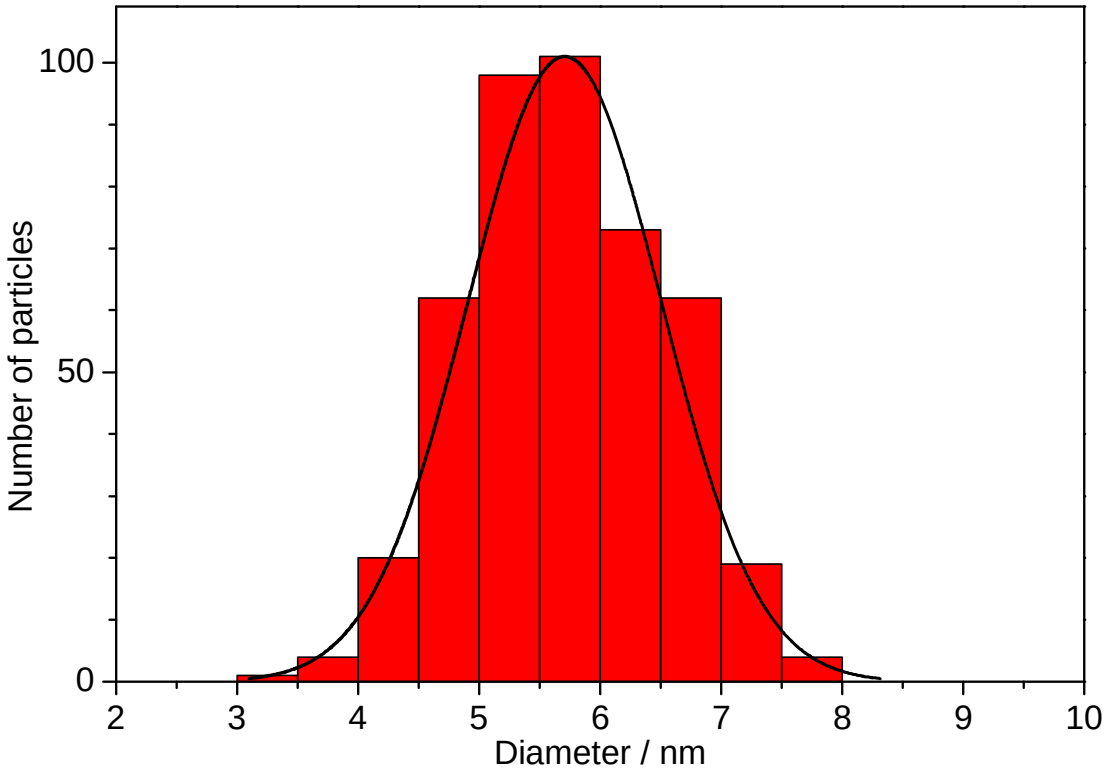

Figure S2. Size histogram of uranium oxide nanodots synthesized in a mixture of BnOBn / OA / OAm / $UO_2(NO_3)_2$*$6H_2O$. The synthesis was performed under Ar atmosphere according to the following heating up process: 220°C-30 min, 280°C-30 min.

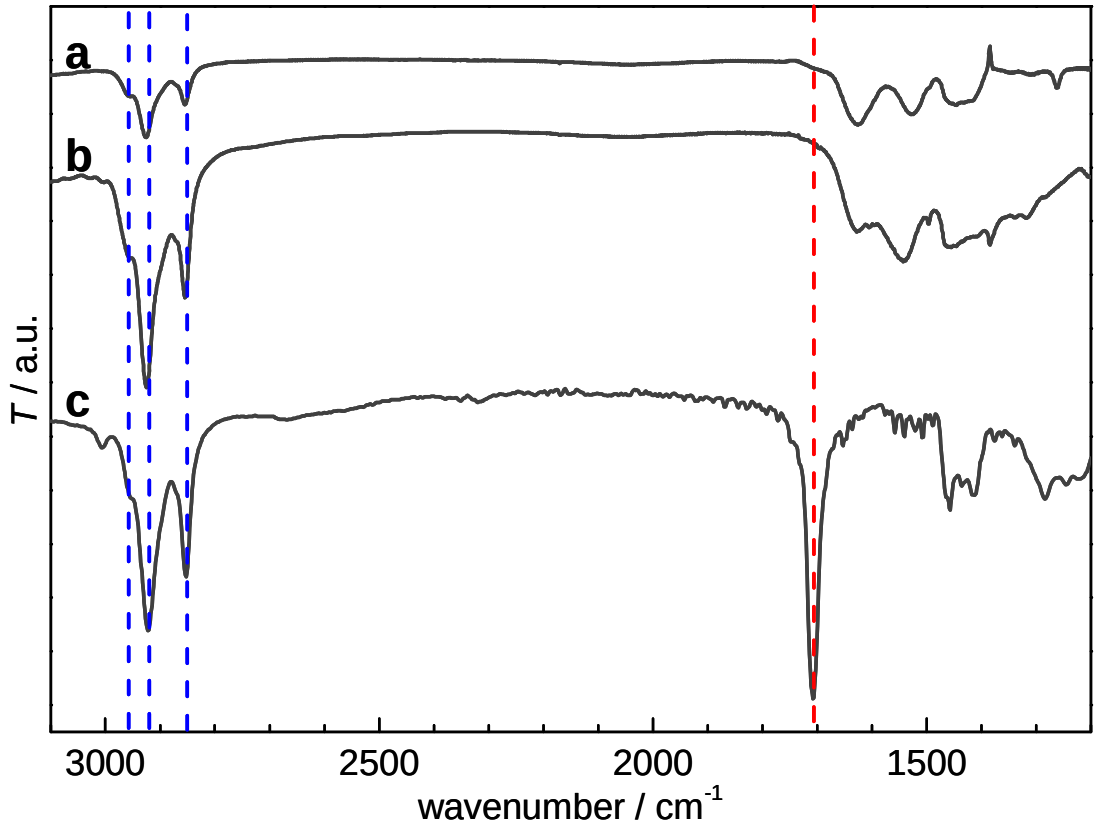

Figure S3. FTIR spectra of (a) uranium oxide and (b) neptunium oxide nanodots synthesized in a mixture BnOBn / OA / OAm with $UO_2(NO_3)_2.6H_2O$ and $NpO_2(NO_3)_2.3H_2O$ as actinide precursors respectively. All syntheses were performed under Ar atmosphere according to the following heating up process: 220°C-30 min, 280°C-30 min. The FTIR spectrum of pure OA is also shown (c).

In the case of oleic acid (Figure S3c), strong absorptions at 2853 and 2922 cm^{-1} are characteristic of the symmetric and asymmetric C-H stretches. The weak absorption at 2956 cm^{-1} is attributed to the asymmetric stretching of the terminal methyl moiety of the alkyl chain whereas the very weak absorption at 3007 cm^{-1} results from the olefin stretching. The very strong absorption at 1708 cm^{-1} is characteristic of the stretching vibrations of the carboxyl group. Absorptions at 1461 and 1284 cm^{-1} are attributed to the O-H in-plane and C-O

vibrations, respectively. The FTIR spectra of the as-prepared uranium oxide nanocrystals (Figure S3a) and neptunium oxide nanocrystals (Figure S3b) are very similar to the one of pure OA but exhibit clear evidence of oleate coordination. The carboxyl stretching absorption at 1708 cm^{-1} disappears whereas two new absorptions at 1415 and 1523 cm^{-1} (uranium sample) or 1420 and 1540 cm^{-1} (neptunium sample) are observed. These bands are characteristic of the asymmetric and symmetric stretching vibrations of a metal coordinated carboxylate group *[Appl. Surf. Sci. 2006, 253, 2611-2617]*.

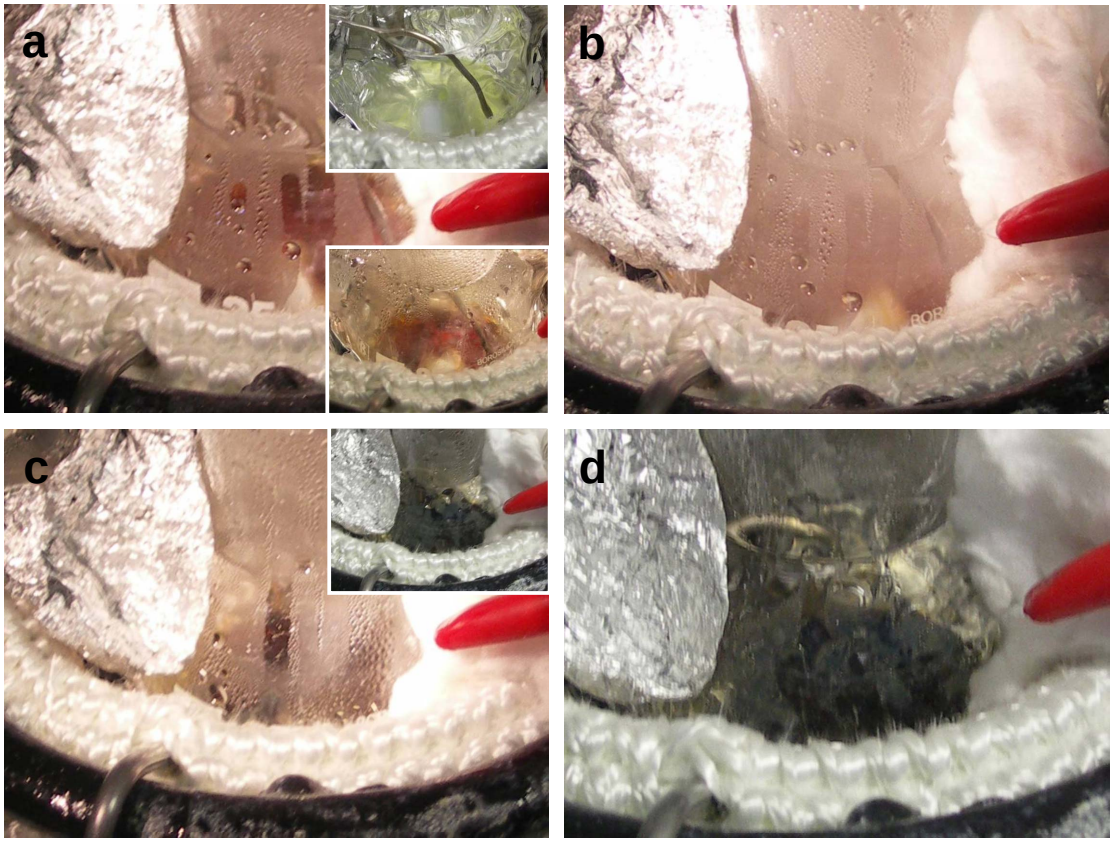

Figure S4. Pictures of the reactive mixture $UO_2(NO_3)_2$*$6H_2O$ / BnOBn / OA / OAm at various moments during the heating up process. Pictures have been taken at 100°C (a), 150°C (b), 220°C (c) and 280°C (d). Insets in picture (a) show the reactive mixture immediately after adding the uranyl precursor (upper part) as well as after ist dissolution (lower part). Inset in picture (c) shows the reactive mixture after 30 min at 220°C.

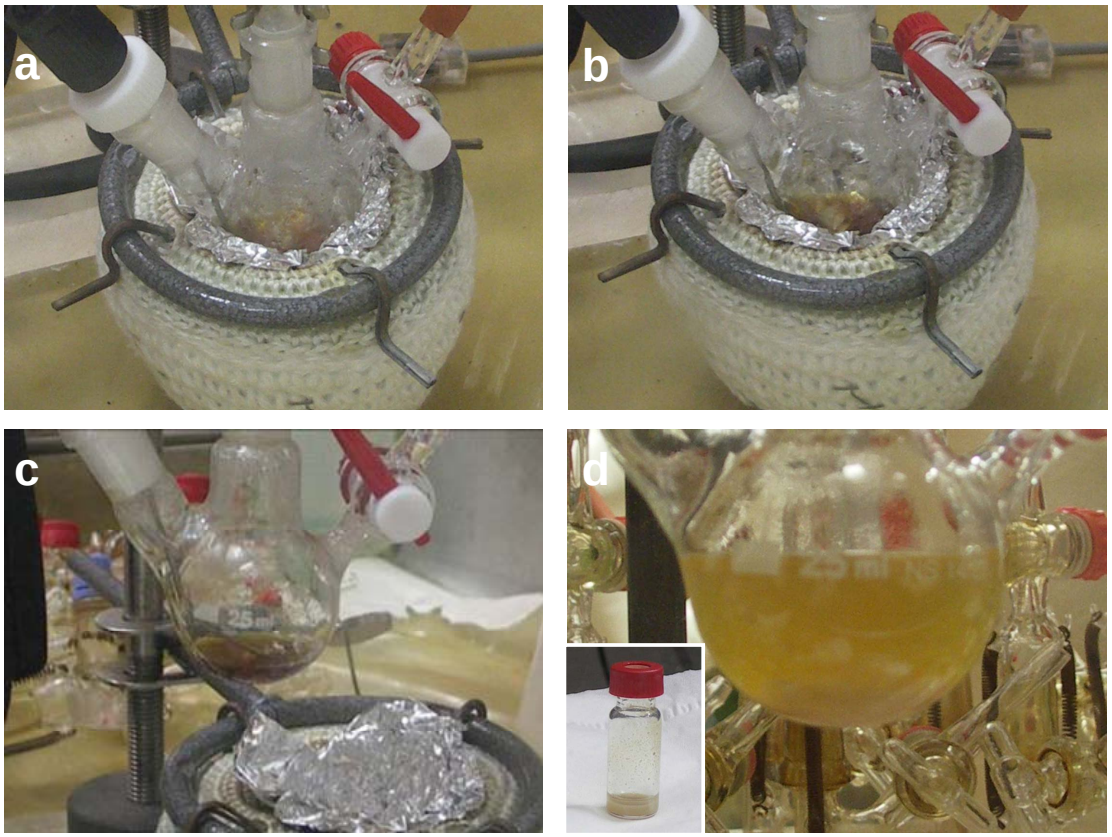

Figure S5. Pictures of the reactive mixture $NpO_2(NO_3)_2$*$3H_2O$ / BnOBn / OA / OAm at various moments during the heating up process. Pictures have been taken at 100°C (a), 220°C (b) and 280°C (c). Picture of the evolution of the reactive mixture during the extraction procedure (i.e. ethanol precipitation) is shown in (d). Inset in picture (d) shows, after three washing steps, the purified precipitate in ethanol.

a / Å	5.4348 (8)
C_{size} / nm	5.4
U_{iso} U / Å^2	0.0402 (4)
U_{iso} O / Å^2	0.089 (4)
Rp	3.25
Rwp	4.15
GOF	5.38

Table S1. Final results of the Rietveld refinements of uranium oxide nanodots synthesized in a mixture of $UO_2(NO_3)_2.6H_2O$ / BnOBn / OA / OAm. The synthesis was performed under Ar atmosphere according to the following thermal profile: 220°C - 30 min, 280°C - 30 min. The lattice parameters, crystallite sizes and isotropic atomic displacement parameters as well as the values of reliability (Rp, Rwp and GOF) are given.

a / Å	5.4317 (6)
C_{size} / nm	4.0
U_{iso} U / Å^2	0.0091 (2)
U_{iso} O / Å^2	0.015 (2)
Rp	2.20
Rwp	3.22
GOF	4.26

Table S2. Final results of the Rietveld refinements of neptunium oxide nanodots synthesized in a mixture of $NpO_2(NO_3)_2.3H_2O$ / BnOBn / OA / OAm. The synthesis was performed under Ar atmosphere according to the following thermal profile: 220°C - 30 min, 280°C - 30 min. The lattice parameters, crystallite sizes and isotropic atomic displacement parameters as well as the values of reliability (Rp, Rwp and GOF) are given.